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Dissociation energies, r-centroids and Franck-Condon factors of AsS molecule

Miss Ashrafuaaisa, D. V. K. Rao and P. T. Rao

Department of Physics, Andhra University, Waltair 530003

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True potential energy curves of $X^2\pi_{3/2}$ and $A'^2\pi_{3/2}$ states of AsS molecule have been constructed by RKRV method from band spectroscopic data. Franck-Condon factors and r-centroids useful in the study of the relative transition probabilities are determined for the $A'^2\pi_{3/2}-X^2\pi_{3/2}$ system. It has been concluded that the (0, 0) band of the system cannot be observed owing to negligible small Franck-Condon factor. The dissociation energies of the lower and upper states of the molecule are estimated by using the three parameter Lippincott function, Hulburt and Hirschfelder function and electronegativity function suggested by Szoke and Baitz. The dissociation products in the upper and lower states of the above system of AsS molecule are determined.

1. Introduction

Recently the band spectrum of AsS molecule in the region $\lambda\lambda$4300–7000 Å has been reported by Shimauchi (1969). From a detailed vibrational analysis, the bands have been attributed to $A'^2\pi_i-X^2\pi_r$ system. Rotational analysis for same bands of $A'^2\pi_{3/2}-X^2\pi_{3/2}$ sub-system has been carried out by Shimauchi *et al* (1971, 1973).

As the construction of accurate potential energy curves for diatomic interaction is of fundamental importance in chemical physics for the understanding of various physical problems arising in gas kinetics and molecular spectra, an attempt has been made to calculate true potential energy curves and dissociation energies of $X^2\pi_{3/2}$ and $A'^2\pi_{3/2}$ states. A knowledge of the vibrational band strengths is required in order to relate experimental intensity data to relative vibrational level populations within the excited states. Hence Franck-Condon factors are r-centroids of $A'^2\pi_{3/2}-X^2\pi_{3/2}$ system of the AsS molecule have been computed. The spectroscopic data of the $X^2\pi_{3/2}$ and $A'^2\pi_{3/2}$ states are taken from Shimauchi *et al* (1973).

2. The True Potential Energy Curves

The potential energy curves for $A'^2\pi_{3/2}$ and $X^2\pi_{3/2}$ states of AsS molecule are constructed by using Rydberg-Klein-Rees method as modified by Vanderslice

et al (1959, 1960). The turning points of nine vibrational levels of the lower state and seven vibrational levels of the upper state are determined and presented in tables 1 and 2 along with their U and $U+T_e$ values. The potential energy curves of the upper and lower states have also been computed by using Morse (1929) analytical function to test the validity of Morse potential for these states. The deviation of Morse potential curves of the lower and upper states from the true potential energy curves can be seen from tables 1 and 2.

Table 1. True potential energy curves of the ground ($X^2\pi_{3/2}$) state of AsS molecule.

V	$U(r)$cm^{-1}	RKRV Values		Morse Function	
		r_{min}(Å)	r_{max}(Å)	r_{min}(Å)	r_{max}(Å)
0	276.76	1.967	2.069	1.968	2.070
1	827.40	1.934	2.111	1.935	2.112
2	1374.20	1.912	2.142	1.913	2.143
3	1917.16	1.895	2.167	1.896	2.168
4	2456.28	1.881	2.191	1.882	2.192
5	2991.56	1.868	2.212	1.869	2.213
6	3523.00	1.857	2.232	1.858	2.233
7	4050.60	1.847	2.251	1.848	2.252
8	4574.36	1.838	2.269	1.839	2.269
9	5094.28	1.829	2.286	1.830	2.287

ble 2. True potential energy curves of the $A'^2\pi_{3/2}$ state of AsS molecule

V	$U(r)$cm^{-1}	$(U+T_e)$cm^{-1}	RKRV Values		Morse Function	
			r_{min}(Å)	r_{max}(Å)	r_{min}(Å)	r_{max}(Å)
0	198.34	18893.44	2.191	2.311	2.192	2.313
1	593.42	19388.52	2.151	2.361	2.153	2.362
2	986.36	19681.46	2.126	2.397	2.127	2.398
3	1377.16	20072.26	2.106	2.427	2.107	2.428
4	1765.82	20460.92	2.089	2.454	2.090	2.455
5	2152.34	20847.44	2.074	2.479	2.075	2 480
6	2536.72	21231.82	2.061	2.502	2.062	2.503
7	2918.96	21614.06	2.049	2.524	2.050	2.525

3. Dissociation Energies

The true potential energy curves for a molecular electronic state have been used to estimate the dissociation energies of diatomic molecules in a number of cases by fitting an empirical potential energy curve to the true potential energy curves. In a comparative study of empirical internuclear potential functions Steele *et al* (1962), have shown that the five parameter Hulburt and Hirschfelder function gives the potential curve with an average error of 1 to 2% in $(V-V_{RKR})/D_0$. Very recently Szoke & Baitz (1968) have also suggested an empirical function depending on the electronegativity of the constituent atoms to represent the potential energy curve of diatomic molecule. This potential function has been found to give a quite a good fit to the true potential curve as measured by $(V-V_{RKR})/D_0$ throughout the useful range of the r values. Hence in order to estimate the dissociation energies of the ground $X^2\pi_{3/2}$ and the excited $A'^2\pi_{3/2}$ states of AsS molecule, the five parameter Hulburt-Hirschfelder function and electronegativity function given by Szoke and Baitz are used. Since in some cases (Singh & Rai 1965) the three parameter Lippincott function (Lippincott & Steele 1961) is found to give a good fit to the RKRV curves, an attempt has been made to test its validity in the present study. The dissociation energies are found to be 32,000 cm^{-1} (3 967 ev) and 24,000 cm^{-1} (2.976 ev) for the ground and upper states respectively. The U_{min} and U_{max} values from each of these functions are compared with the true U values in tables 3 and 4. The dissociation products in the upper state are determined from the atomic excitation energies by using the relation

$$T_e+D_e' = D_e''+\text{sum of atomic excitation energies.}$$

The most probable products of dissociation for the upper state are determined as an excited As (^2D) atom, $S(^3P)$ atom in the ground state. The ground state is assumed to dissociate into an unexcited combination of As(^{4}S)+S(^{3}P) atoms.

4. r-Centroids

The r-centroid $(r_{v',v''})$ of a $(v'-v'')$ transition has been defined by Nicholls & Jarmain (1956). The r-centroids of $A'^2\pi_{3/2}-X^2\pi_{3/2}$ system of AsS molecule have been evaluated by both graphical and quadratic methods suggested by Nicholls & Jarmain (1956). The results are presented in table 5. A smooth curve has been obtained when a graph was drawn between $r_{v',v''}$ and $\lambda_{v',v''}$, as was observed by Nicholls & Jarmain (1956). The sequence difference

$$\Delta\tilde{r} = \tilde{r}_{v'+1,\, v''+1}-\tilde{r}_{v',\, v''}$$

for the system is found to be constant. As Δr of this system is less than 0.01 Å, it is concluded that the potentials are not wide. The fact that the $r_{0,0}$ is found to be slightly less than the $\frac{1}{2}(r_{e_1}+r_{e_2})$ indicated that the potentials are anharmonic.

5. Franck-Condon Factors

The relative transition probability of a v', v'' band is

$$P = R_e^2(r_{v',v''}) \left| \int \psi_{v'} \psi_{v''} dr \right|^2 = R_e^2(r_{v',v''}) q_{v',v''},$$

where R_0 is the electronic transition moment, $\psi_{v'}$ and $\psi_{v''}$ are the vibarational

Table 3. Dissociation energy of the ground $X^2\pi_{3/2}$ state of AsS molecule

V	U cm^{-1}	Lippincott function D = 32000 cm^{-1} (3.3967 ev)		H-H function D = 32000 cm^{-1}		Electronegativity function D = 32000 cm^{-1}	
		U_{min}cm^{-1}	U_{max}cm^{-1}	U_{min}cm^{-1}	U_{max}cm^{-1}	U_{min}cm^{-1}	U_{max}cm^{-1}
0	276.76	346.56	256.23	291.9	263.1	290.1	264.75
1	827.40	825.04	786.12	847.2	806.5	838.20	815.58
2	1374.20	1368.70	1325.97	1405.5	1358.9	1386.3	1379.2
3	1917.16	1900.5	1838.30	1952.1	1881.8	1920.1	1915.7
4	2456.28	2417.4	2385.73	2483.7	2439.0	2437.2	2490.1
5	2991.56	2965.3	2903.61	3047.9	2964.5	2983.7	3034.3
6	3523.00	3482.8	3426.31	3581.5	3493.2	3498.5	3584.2
7	4050.60	3998.16	3946.24	4113.5	4017.5	4009.9	4131.6
8	4574.36	4500.01	4457.19	4632.1	4531.0	4506.9	4669.7
9	5094.28	5039.26	4954.10	5190.9	5028.8	5039.9	5193.2

Table 4. Dissociation energy of the upper $A'^2\pi_{3/2}$ state of AsS molecule

V	U cm^{-1}	Lippincott function D_0 = 24000 cm^{-1} (2.976 ev)		H-H function D_0 = 24000 cm^{-1}		Electronegativity function D_0 = 24000 cm^{-1}	
		U_{min}cm^{-1}	U_{max}cm^{-1}	U_{min}cm^{-1}	U_{max}cm^{-1}	U_{min}cm^{-1}	U_{max}cm^{-1}
0	198.34	211.39	187.56	205.5	188.80	204.2	189.61
1	593.42	622.75	579.40	614.7	583.7	607.5	587.80
2	986.36	991.32	968.56	1001.8	976.4	985.66	984.8
3	1377.16	1375.94	1350.22	1393.30	1361.9	1365.2	1375.1
4	1765.82	1811.77	1732.18	1839.2	1747.9	1794.1	1766.5
5	2152.34	2152.06	2114.22	2189.0	2134.1	2128.1	2158.5
6	2536.72	2528.39	2486.85	2577.6	2510.9	2496.8	2541.3
7	2918.96	2909.20	2859.99	2972.7	2888.1	2869.1	2925.0

wave functions of the molecule in the v' and v'' states and $q_{v',v''}$ denotes the Franck-Condon factor for the v'–v'' transition. In the present case as the value $|d\alpha/\alpha|$ for $A'^2\pi_{3/2}-X^2\pi_{3/2}$ system of AsS molecule is found to be 29.5% the Franck-Condon factors have therefore been evaluated by analytical method of Fraser & Jarmain (1953) with r_e-shift correction. For each band a set of ρ_1 and ρ_2 values and (0, 0) integral are computed for the evaluation of Franck-Condon factors. The Franck-Condon factors for $(v'+v'') < 10$ are displayed in table 5.

Table 5. Frank-Condon fractors and r-centroids of $A'^2\pi_{3/2}-X^3\pi_{3/2}$ system of AsS molecule

V'/V''	0	1	2	3	4	5	6
0*a*	0.0001	0.0015	0.0073	0.0232	0.0535	0.0952	...
b	2.1258	2.1420	2.1585	2.1750	2.1918	2.2090	2.2265
c	2.1260	2 1410	2.1570	2.1730	2.1890	2.2060	2.2230
d	...	...	5535.20	5710.00	5895.00	6092.00	6301.50
1*a*	0.0011	0.0085	0.0320	0.0731	0.1107	0.1128	...
b	2 1180	2.1305	2.1465	2.1625	2.1790	2.1960	2.2030
c	2.1150	2.1300	2.1460	2.1622	2 1770	2.1940	2.2100
d	...	5255.20	5413.50	5581.00	5758.00	5946.00	6145.00
2*a*	0.0040	0.0253	0.0691	0.1037	0.0848	0.0268	...
b	2.1030	2.1190	2.1350	2.1510	2.1670	2.1840	2.2000
c	2.1050	2.1195	2.1347	2.1500	2.1660	2.1819	2.1980
d	...	5146.60	5298.50	5558.50	5628.00	5807.00	...
3*a*	0.0106	0.0505	0.0949	0.0798	0.0182	0.0049	...
b	2.0930	2.1080	2.1240	2.1400	2.1550	2.1720	2.1880
c	2.0941	2.1089	2.1239	2.1391	2.1546	2.1704	2.1864
d	...	..	5189.50	5343.00	...	...	...
4*a*	0.0220	0.0761	0.0893	0.0280	0.0029	...	...
b	2.0830	2.0970	2.1120	2.1270	2.1440	...	...
c	2.0840	2.0986	2.1133	2.1284	2.1436	...	...
d	...	4943.90	5084.10	5231.60	...	...	...
5*a*	0.0376	0.0913	0.0501	0.0003	...	...	...
b	2.0720	2 0870	2.1020	2.1170	...	...	...
c	2.0741	2.0884	2.1030	2.1178	...	...	...
d	4721.00	4848.80	4983.20	...	...	...	...
6*a*	...	...	...	...	...	...	...
b	2.0620	2.0760	...	...	...	...	...
c	2.0644	2.0785	...	...	...	...	...
d	4633.40	4758.90	...	...	...	...	...

a) Franck-Condon factors, *b*) and c) $r_{v',v''}$ by graphical and quadratic methods respectively in A. *d*) Wavelength of the bands in A. U.

From the study of Franck-Condon factors of $A'^2\pi_{3/2}-X^2\pi_{3/2}$ system, the absence of (0, 0) band is readily explained as due to the negligibly small value of the Franck-Condon factor. A number of heads are expected in both v' and v'' progressions in accordance with the vibrational sum rule (Herzberg 1950).

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Fraser P. A. & Jarmain W. R. 1953 *Proc. Phys. Soc.* **A66**, 1153.
Herzberg G. 1950 *Spectra of Diatomic molecules*, Van Nostrand, New York.
Hulburt H. M. & Hirschfelder 1961 *J. Chem. Phys.* **35**, 1901.
Lippincott E. R. & Steele D. 1961 *J. Chem. Phys.* **35**, 2068.
Morse P. M. 1929 *Phys. Rev.* **34**, 57.
Nicholls R. W. & Jarmain W. R. 1956 *Proc. Phys. Soc.* **A69**, 253.
Shimauchi M. 1969 *Science of Light* **18**, 90.
Shimauchi M. 1971 *Can. J. Phys.* **49**, 1249.
Shimauchi M., Sakaba Y. & Kikuchi S. 1972 *Science of Light* **21**, 1.
Shimauchi M. & Karasawa S. 1973 *Science of Light* **22**, 127.
Steele D., Lippincott E. R. & Vanderslice J. T. 1962 *Rev. Mod. Phys.* **34**, 239.
Singh R. B. & Rai D. K. 1965 *Can. J. Phys.* **43**, 829.
Szoke S. & Baitz 1968 *Can. J. Phys.* **46**, 2563.
Vanderslice J. T., Mason E. A., Maisch W. G. & Lippincott E. R. 1959 *J. Mol. Spec.* **3**, 17.
Vanderslice J. T., Mason E. A., Maisch W. G. & Lippincott E. R. 1960 *J. Mol. Spect.* **5**, 83